JOURNAL OF CATALYSIS **84,** 248–251 (1983)

On the Mechanism of Fischer–Tropsch Synthesis on a Single Crystal Nickel Catalyst

In the past several years there has been renewed interest in the mechanism of the catalytic synthesis of methane and higher molecular weight hydrocarbons (HHC) when H_2 and CO interact over transition metal catalysts. Recent experimental work as well as 50 years of mechanistic proposals have been reviewed extensively, most recently by Bell (*1*). Most of the mechanistic discussion concerns whether or not CO is directly involved in the chain building process. Ponec (*2*) has reviewed the arguments suggesting the involvement of adsorbed molecular CO in the synthesis of higher hydrocarbons. Bell's review (*1*) summarizes the recent work which has led to the now widely held view that the non-methane hydrocarbon synthesis is the result of the polymerization of partially hydrogenated carbon atoms. We report here measurements on a model (single crystal) Ni catalyst of the product distribution and the surface "carbide" concentration as the gas phase pressure of CO varied over a wide range. The ability to determine under reaction conditions the coverage of active surface carbon (for a range of coverages from 10 to 50% of a monolayer, the highest possible without deactivation of the surface) and to relate those measurements to product yields (spanning a range of three orders of magnitude) allows us to conclude that adsorbed molecular CO is directly involved in higher hydrocarbon synthesis.

In previous publications (*3–5*), we have demonstrated the equivalence of H_2/CO reaction rates measured over Ni (100) with those measured over supported Ni catalysts. This work also provided revealing information on the reaction mechanism for methane synthesis. The key to the mechanistic conclusions was the ability to measure the surface carbon concentration and to relate this measurement to surface concentrations under steady-state reaction conditions. Detailed descriptions of the apparatus, the crystal cleaning procedures, the techniques used to obtain kinetic rate data, and the surface analytical procedures (primarily Auger Electron Spectroscopy (AES)) are included in Ref. (*4*).

As has been demonstrated previously (*6*), the specific rate of CH_4 formation over a Ni(100) catalyst fits a smooth curve when plotted against the measured surface carbon concentration on the crystal surface. Figure 1, which includes additional data beyond that given in Fig. 3 of Ref. 6, illustrates this behavior for a wide range of total pressure and H_2/CO ratios. It must be emphasized that the reaction rates are highly reproducible steady-state catalytic rates with no measurable time dependence and that the surface carbon concentration (a "carbide" species (*3*)) at constant reaction conditions is independent of reaction time. The correlation indicated in Fig. 1 between surface carbide level and the specific rate of CH_4 formation is consistent with, and adds further support to, the mechanism of the methanation reaction previously proposed (*4*). In this mechanism the overall rate of CH_4 production is determined by a balance of two surface reactions:

$$(CO)_{ads} \rightarrow C_{ads} + O_{ads} \qquad (1)$$

$$C_{ads} + 4H_{ads} \rightarrow CH_4 \qquad (2)$$

The coverage of surface carbon (C_{ads}) and hydrogen (H_{ads}) are determined by both the rate of CO dissociation and the rate of hydrogenation of the surface carbide. Since

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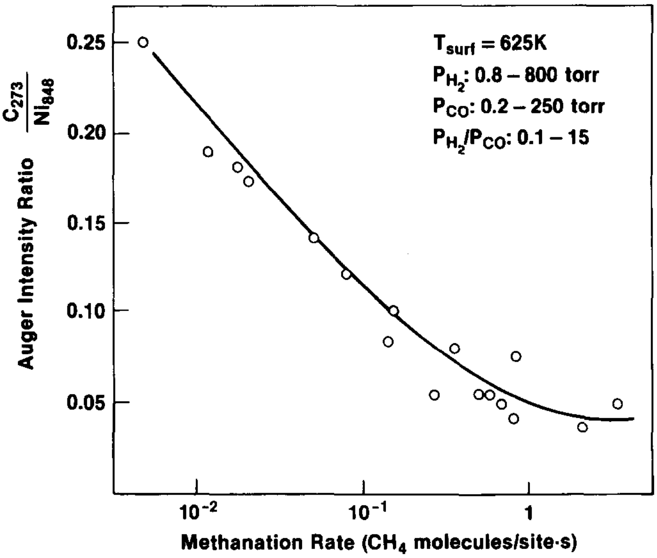

FIG. 1. Methanation rate versus steady-state surface carbon level on a Ni(100) surface. The methanation rate is expressed as a turnover number and the carbon level is given as a ratio of the C_{273} and Ni_{848} peak-to-peak Auger signal intensities. By correlating Auger and LEED measurements it has been estimated that a ratio of $C_{273}/Ni_{848} = 0.25$ corresponds to a carbide saturation coverage of $\theta_c \simeq 0.50$.

these surface coverages are pressure dependent, varying the partial pressure of either H_2 or CO has the kinetically important effect of altering the relative coverages of both C and H atoms, and thereby affects the rate of methane production. If under steady-state reaction conditions, the coverage of C_{ads} is constant and the rate of CH_4 production is constant then the H_{ads} coverage must also be constant, provided reaction (2) is the only source of CH_4.

While methane is the dominant reaction product on nickel catalysts, higher molecular weight hydrocarbons (HHC) are always produced with yields which change with reaction conditions. We have investigated HHC synthesis by measuring the total hydrocarbon product as a function of the pressure of CO, while holding the surface carbide coverage at a fixed value. This was accomplished by adjusting the partial pressure of H_2 for each pressure of CO to achieve the desired surface carbide level. Thus, the H_2/CO ratio is changed for each experiment but the surface carbide is maintained at a nearly constant value; the partial pressure of CO is known, and the rate of production of both CH_4 and HHC are measured. It must be emphasized that as Fig. 1 shows the H_2/CO ratio is only one of a number of factors (the total pressure and reaction temperature being crucially important)

TABLE 1

Reaction Conditions and Turnover Numbers for Production of Methane and Higher Hydrocarbons on a Ni(100) Surface

AES ratio	Torr		$N_{CH_4} \times 10^2$	$N_{HHC} \times 10^2$
	P_{co}	P_{H_2}		
(a) $\frac{C_{273}}{Ni_{848}} = 0.05 \pm 0.01$	2	30	77.1	0.025
	10	40	47.1	0.030
	24	96	66.2	0.090
	250	256	49.2	0.451
(b) $\frac{C_{273}}{Ni_{848}} = 0.18 \pm 0.01$	1	3.7	1.09	0.0034
	5	5	1.56	0.005
	100	10	1.40	0.024

Note. N_x = molecules of x/site · s.

in determining surface coverages and reaction rates. Two series of experiments were conducted at a surface temperature of 625 K, one at low carbide coverage and the other at high carbide coverage. The results of these experiments are tabulated in Table 1 and plotted in Fig. 2. Two features of the data in Fig. 2 should be emphasized: (1) When reaction conditions are adjusted to produce the higher surface carbide level (Fig. 2b) the rate of production of both CH_4 and HHC are depressed compared with the low carbide regime (Fig. 2a). (2) At both high and low carbide concentrations (i.e., all reaction conditions of Fig. 2), the rate of methane production is independent of P_{CO}, while the rate of higher hydrocarbon production strongly depends on P_{CO}. A mechanism for hydrocarbon chain growth proceeding predominantly through the polymerization of partially hydrogenated carbon species is incompatible with these observations. Any surface carbon polymerization (whatever the detailed mechanism) will result in an increased fraction of HHC products when the surface carbon concentration is increased. Figure 2 shows that the gas phase pressure of CO is the dominant influence on the HHC production rate at both low and high surface carbon coverages. The constant methanation rate, the constant carbide level, and the inferred constant surface hydrogen concentration demand that another surface species is involved in higher hydrocarbon production. The strong dependence of HHC yields on the gas pressure of CO suggests that this other species is a pressure-dependent form of chemisorbed CO. Temperature-programmed desorption (TPD) studies of the

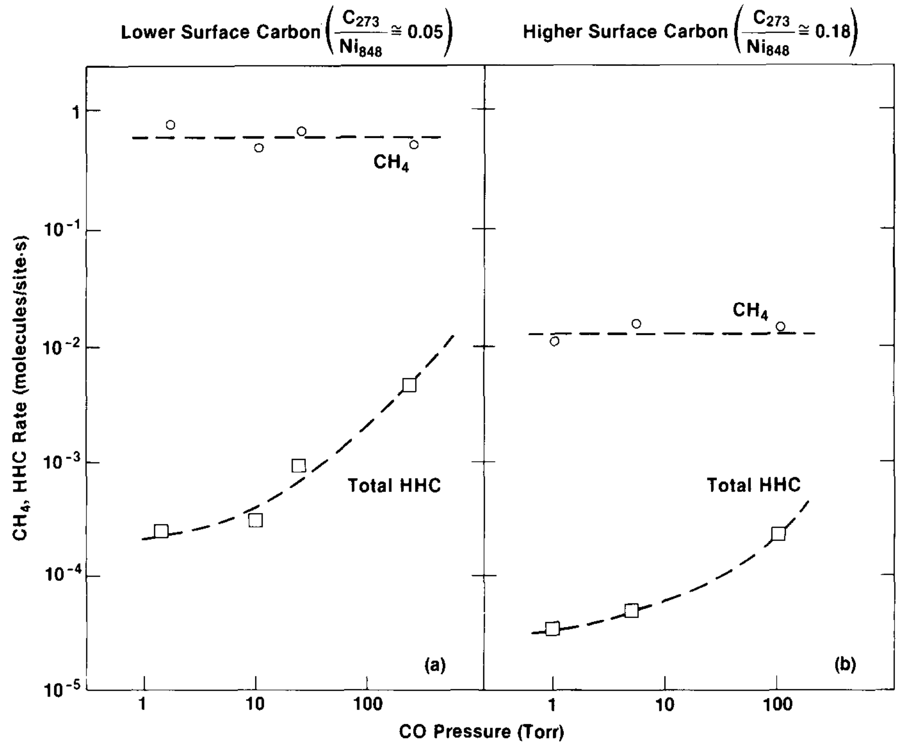

FIG. 2. Rate of methane and higher hydrocarbon (HHC) production versus the CO reactant pressure on a Ni(100) surface. Rates are expressed as turnover numbers, and the HHC production includes the total measured yield for C_2, C_3, and C_4 species. The estimated coverage of surface carbide is (a) 0.10 and (b) 0.35.

chemisorption of CO on single crystals of nickel (*7*) indicate that a nickel surface saturated with carbon monoxide contains molecular CO, a large fraction of which is strongly bound and substantially pressure-independent (β-CO in TPD), and a small fraction of which is weakly bound and pressure-dependent (α − CO). We suggest that the β-CO is the precursor to the surface carbide (see Fig. 1 of Ref. (*5*) for the pressure dependence of the CO dissociation reaction on Ni(100)) and that higher hydrocarbons are produced by the interaction of chemisorbed α-CO with the partially hydrogenated carbide species. Since α-CO is a high coverage species, large changes in pressure are required to produce relatively small increases in the concentration of α-CO (*7*). A mechanism similar to this has been proposed by Ponec (*2*), and earlier by Pichler and Buffleb, (*8*) and Sternberg and Wender (*9*), in which adsorbed molecular CO inserts into the metal–carbon bond of a CH_x species leading to higher hydrocarbons.

As a final note, it should be pointed out that all of the experiments (*1*) which have led to the suggestion of a carbon polymerization mechanism for HHC production involved the deposition of carbon and its subsequent removal in either H_2 or H_2/CO gas mixtures. By using a variety of deposition techniques, these experiments have clearly shown that the polymerization of partially hydrogenated carbon atoms occurs on transition metal catalysts; however, the kinetic importance of this process for steady-state H_2/CO reactions on surfaces which have not been predosed with carbon has not been demonstrated. The present data indicate that under steady-state reaction conditions the HHC production rate is dominated by a CO insertion mechanism.

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Received December 17, 1982